

The effect of biomass pyrolysis gas reburning on N₂O emission in a coal-fired fluidized bed boiler

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Received October 30, 2009; accepted July 6, 2010

The fossil fuel consumption and pollutant emissions in a coal fired fluidized bed boiler could be reduced by biomass pyrolysis gas reburning. The influence of three kinds of biomass pyrolysis gases on the emission of N₂O in a laboratory scale fluidized bed was investigated using the mechanism of GRI3.0 in this paper. The results showed that: the effect of sawdust pyrolysis gas reburning on N₂O was more significant than that of rice husk and orange peel under the same conditions; the increase of initial oxygen content from 1% to 8% in flue gas would restrain the decomposition of N₂O; the N₂O decomposition was enhanced by increasing reaction temperature from 1073.15 K to 1323.15 K, and the decomposition rate may reach 99% at 1223.15 K.

biomass pyrolysis gas, reburning, nitrous oxide (N₂O), pollutant emission, fluidized bed

Citation: Hu X Y, Dong C Q, Yang Y P, et al. The effect of biomass pyrolysis gas reburning on N₂O emission in a coal-fired fluidized bed boiler. *Chinese Sci Bull*, 2011, 56: 1429–1433, doi: 10.1007/s11434-010-4145-9

Biomass fuels is a form of renewable energy source, which can be considered CO₂ neutral fuels and giving lower emissions of SO₂, NO_x, and heavy metals respect to coals. NO_x emissions could be reduced by using biomass, which contains low nitrogen and high volatile content [1–3]. As a normal power generation technology, biomass co-firing was initiated in Europe and the United States in the 1980s. Now there are more than 150 biomass co-firing power generation projects in the world [4,5]. This technique can reduce the emissions of NO_x and CO₂ with lower fuel costs [6]. The typical biomass includes sawdust, agricultural wastes, animal wastes and anthropomorphic wastes. The most popular approaches to biomass utilization in electric power generation include [4,7–11]:

(1) Blending biomass with coal on the fuel pile: biomass and coal are mixed first, then milled and injected into the boiler combustor;

(2) Co-firing with separate injection: biomass and coal are mixed and burned in the boiler after being injected into the boiler separately;

(3) Gasification-based co-firing (also named reburning):

biomass is gasified first and then injected into the boiler for burning together with the waste gas produced from coal combusting.

Compared with indirect co-firing, there are some disadvantages for blending biomass with coal on the fuel pile and co-firing with separate injection [5,12]:

(1) With various shapes, biomass is difficult for fragmentation and may cause plugging in bunkers;

(2) Biomass contains high alkali metal and chlorine content, which may cause slagging and corrosion in coal-fired boilers with coal and have effect on the utilization of co-firing ash;

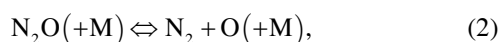
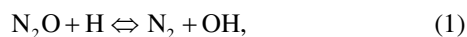
(3) Co-firing of biomass with coal may result in the deactivation of catalysts in denitration system.

In recent years, the large-scale coal-fired circulating fluidized bed (CFB) has been developed at a very fast pace with some problems correspondingly. As a greenhouse gas, N₂O concentration produced in CFB is about 39 to 589 mg N⁻¹ m⁻³, sometimes as high as 786 mg N⁻¹ m⁻³, while it is generally less than 20 mg N⁻¹ m⁻³ in traditional pulverized coal boiler [13,14]. The radial H produced in the process of fuel gas reburning has significant serious influence on N₂O

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reduction [15]. The combustible material of biomass pyrolysis gas mainly contains H_2 , CH_4 and CO , which are helpful to reduce nitrogen oxide emissions [5, 16, 17]. Because of low alkali metal and chlorine content, the gasified gas for co-firing can avoid most of the problems associated with direct co-firing, such as boiler fouling, corrosion and the utilization of co-firing ash. Therefore, reburning is considered as a promising technology. The effect on NO_x reduction depends on the type of fuel gases. CH_4 and H_2 are more effective than CO , which is enhanced by using catalysis and is influenced by the oxygen content in the flue gas [18–23]. The N_2O emission increases with the increase of excess air coefficient. The effect of strengthening air stage, the circulating material rate of quartz and coal particle was slight. The combustion of high rank coal produced more N_2O [16,13]. Besides, the N_2O emission was also influenced by the flow of fuel gases into the reactor and the feed point of coal [24].

In a small scale fluidized bed reactor, experiments of N_2O emission influenced by biomass pyrolysis gas reburning were carried out by Dong et al. [25,26]. The results showed that: the N_2O decomposition rate was improved by the increase of reburning temperature. With a biomass pyrolysis gas proportion of 1% and a reburning temperature of 1123.15 K, the rate was nearly 100%. The oxygen content of flue gas has a negative effect on N_2O decomposition, which is delayed by the increase of biomass pyrolysis gas. Based on the results above, the following reactions on N_2O reduction by reburning should be given more attention takes the most part in further research [27]:



In this paper, N_2O reduction is influenced obviously by the composition of biomass pyrolysis gas. With varied initial oxygen content, reaction temperature and the ratio of reburning fuel gases, sawdust, rice husk, and orange peel were chosen as the typical agricultural and forestry waste in this research.

1 Objectives and methodology

Reburning gas from sawdust, rice husk, and orange peel is produced by fast pyrolysis process at a temperature of 1123.15 K. Ultimate analysis, proximate analysis and pyrolysis gas components of them were given in [28].

The height of reactor was defined as the distance from the biomass pyrolysis gas inlet to the exhaust gas outlet, which is approximately 90 cm as shown in Figure 1. The construction of the model was based on the experimental part in literature [25,26]. In the chemical reaction process, the following assumptions have been made: (1) Biomass pyrolysis gas and flue gas were mixed perfectly before en-

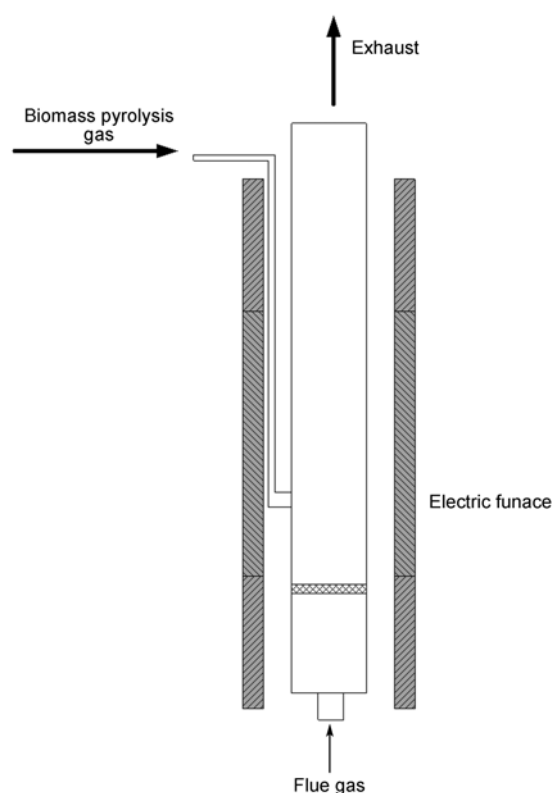


Figure 1 The schematic diagram of biomass pyrolysis gas reburning.

Table 1 Species in the model^{a)}

Species in the model													
H_2	H	O	O_2	OH	H_2O	HO_2	H_2O_2	C	CH	CH_2	$CH_2(S)$	CH_3	CH_4
CO	CO_2	HCO	CH_2O	CH_2OH	CH_3O	CH_3OH	C_2H	C_2H_2	C_2H_3	C_2H_4	C_2H_5	C_2H_6	$HCCO$
CH_2CO	$HCCOH$	AR	N	NH	NH_2	NH_3	NNH	NO	NO_2	N_2O	HNO	CN	HCN
H_2CN	$HCNN$	$HCNO$	$HOCN$	$HNCO$	NCO	N_2	AR	C_3H_7	C_3H_8	CH_2CHO	CH_3CHO		

a) <http://www.me.berkeley.edu/gri-mech/version30/text30.html>.

tering the reaction tube; (2) the influence of mixing in the actual process was ignored; (3) The defined temperature at the inlet of the reactor was reached instantly, and the influence of temperature rise was ignored; (4) The plug flow model was used. The reaction mechanism was based on GRI3.0, which contains 325 chemical reactions and 53 species, whose detail information of species was given at Table 1.

The following equations of N_2O decomposition rate, NO formation rate and NO_2 formation rate were chosen to evaluate N_2O reduction:

$$\eta_{N_2O} = \left(1 - \frac{N_2O_{out}}{N_2O_{in}} \right) \times 100\%, \quad (4)$$

$$\eta_{NO} = \frac{NO_{out}}{2N_2O_{in}} \times 100\%, \quad (5)$$

$$\eta_{NO_2} = \frac{NO_{2out}}{2N_2O_{in}} \times 100\%, \quad (6)$$

where N_2O_{in} and N_2O_{out} are the mole fraction of N_2O before and after the reaction respectively; NO_{out} and NO_{2out} are the mole fraction of NO and NO_2 after the reaction respectively.

2 Results and discussion

2.1 The influence of initial oxygen content

Under the conditions of reaction temperature $T=1173.15$ K, N_2O concentration $c=2800$ ppm, residence time $t=0.17$ s and the fraction content of biomass pyrolysis gas in flue gas $R=1\%$, and varied initial oxygen content, the comparison of the three kinds of biomass pyrolysis gas was shown in Figure 2. The results showed that the reduction effect of sawdust pyrolysis gas was better than that of orange peel and rice husk. The variation trend of different biomass pyrolysis gas influenced by initial oxygen content was consistent. When the initial oxygen content increased from 0 to 3%, the N_2O decomposition rate decreased quickly. With initial oxygen content was above 3%, the decomposition rate become insensitive. In the process of decomposition, the H radical was consumed during the biomass pyrolysis gas reburning process. With the increase of initial oxygen content, H radical reacts with O radical thus decrease the H radical concentration. On the other side, the reverse reaction of $N_2O(+M) \rightleftharpoons N_2+O(+M)$ occurred with oxygen content increased. Additionally, the effect difference of the three kinds biomass pyrolysis gas on N_2O decreased at the same time [25]. Therefore, when biomass pyrolysis gas was used for reburning, higher N_2O decomposition rate could be achieved by choosing initial oxygen content less than 3%.

Using pyrolysis gas of sawdust, rice husk or orange peel, the influence trend of residence time on N_2O was similar. Take sawdust as an example, the effect of residence time and oxygen content on N_2O was shown in Figure 3. Keeping the oxygen content constant, the N_2O decomposition rate increased quickly when residence time varied from 0 s

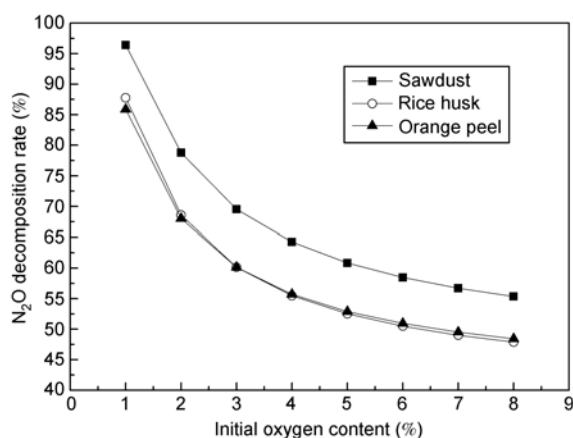


Figure 2 The influence of oxygen content on N_2O decomposition ($T=1173.15$ K, $N_2O/O_2/N_2$, $c_{N_2O}=2800$ ppm, $t=0.17$ s, $R_b=1.0\%$).

to 0.04 s; while it increased slowly when residence time was longer than 0.04 s. Because the residence time in CFB was more than 0.17 s, the N_2O decomposition rate increased slowly with residence time.

2.2 The influence of reaction temperature

As is shown in Figure 4, the N_2O decomposition rate increased along with bed temperature from 1073.15 K to 1323.15 K. With a reburning fuel ratio of 1.0% and a reaction temperature of 1223.15 K, the N_2O reduction remained unchanged, close to complete decomposition. With the change of temperature, the effect of sawdust on N_2O was better than that of rice husk and orange peel.

As is shown in Figure 5, with the increase of reaction temperature, the residence time of stable N_2O decomposition rates was shortened. When the temperature reaches 1273.15 K, the N_2O decomposition rate stayed 99% with a

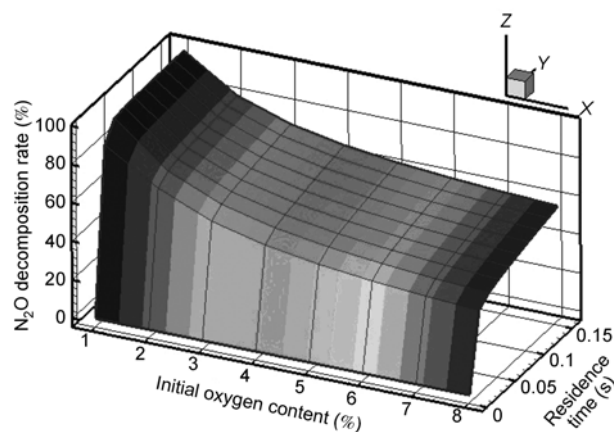


Figure 3 The influence of residence time and oxygen content of flue gas on N_2O decomposition rate (Sawdust, $T=1173.15$ K, $N_2O/O_2/N_2$, $R_b=1.0\%$, $c_{N_2O}=2800$ ppm).

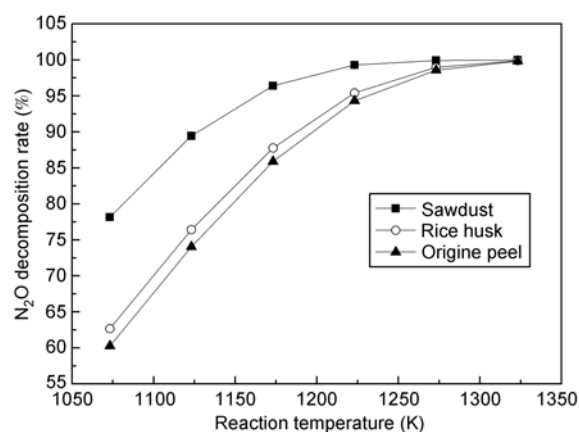


Figure 4 The influence of reburning fuels and reaction temperature on N_2O decomposition ($N_2O/O_2/N_2$, $R_{O_2}=1\%$, $c_{N_2O}=2800$ ppm, $t=0.17$ s, $R_b=1.0\%$).

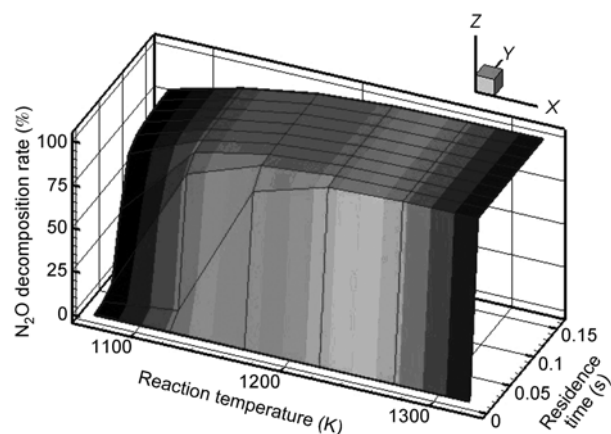


Figure 5 The influence of residence time and reaction temperature on N_2O decomposition rate (Sawdust, $\text{N}_2\text{O}/\text{O}_2/\text{N}_2$, $R_{\text{O}_2}=1\%$, $c_{\text{N}_2\text{O}}=2800$ ppm, $R_b=1.0\%$).

residence time of 0.02 s. The higher the reaction temperature, the more significant the reduction effect on N_2O emission, which was in good agreement with the conclusion in literature [25].

2.3 The influence of biomass gas content

Using pyrolysis gas of sawdust, rice husk or orange peel, the influence trend of biomass pyrolysis gas content of flue gas on N_2O was the same. Taking sawdust for example, Figure 6 (a) showed the change of main species during N_2O reduction process at the temperature of 1173.15 K and the reburning fuel gas ratio of 1%. At the reactor exit, O_2 , H_2O , CO_2 and N_2 were the main species, while the concentration of combustible gases H_2 , CH_4 , CO , C_2H_4 , C_2H_6 , and pollutants N_2O , NO and NO_2 were nearly zero.

All reactions mainly happened in the section of 0–20 cm, where various components of sawdust pyrolysis gas reacted with N_2O . In the process, the mole fractions of H_2O and CO_2 were increased. Figure 6(b) indicated that most of N_2O was decomposed and converted into N_2 , while only a small portion converted into NO and NO_2 . Along with the reaction tube, the NO formation rate increased gradually and remained constant at 2.7%; while the increasing speed of NO_2 formation rate slowed down with a value of 0.015% at the outlet of reactor. In a word, 1.35% of N_2O injected was converted into NO and 0.0075% was converted into NO_2 under the operating conditions.

As is shown in Figure 7, with a certain reaction temperature, N_2O concentration and flue gas composition, N_2O decomposition rate was directly proportional to sawdust pyrolysis gas from 0.1% to 1%, especially at a distance of 0–20 cm. This was consistent with the conclusion in literature [25], where the N_2O decomposition rate increased with reburning fuel ratio from 0.4% to 1.4%.

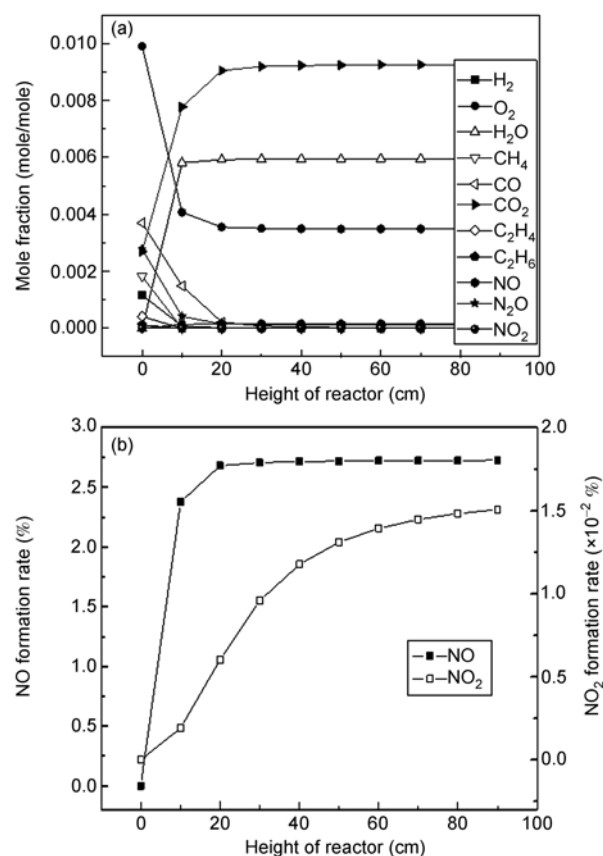


Figure 6 The mole fractions of main species(a) and the formation rate of NO and NO_2 (b) in the reduction process of N_2O (Sawdust, $T=1173.15$ K, $\text{N}_2\text{O}/\text{O}_2/\text{N}_2$, $R_{\text{O}_2}=1\%$, $c_{\text{N}_2\text{O}}=2800$ ppm, $R_b=1.0\%$, $t=0.17$ s).

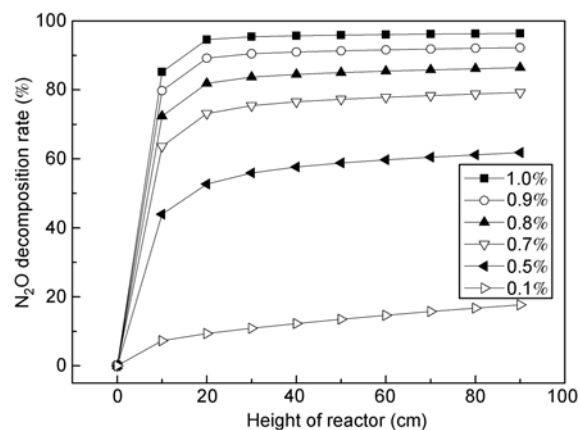


Figure 7 The influence of different pyrolysis gas concentration on N_2O at different position of the reactor (Sawdust, $T=1173.15$ K, $\text{N}_2\text{O}/\text{O}_2/\text{N}_2$, $R_{\text{O}_2}=1\%$, $c_{\text{N}_2\text{O}}=2800$ ppm, $t=0.17$ s).

3 Conclusions

Based on the studies about the influence of pyrolysis gas of sawdust, rice husk and orange peel on N_2O reduction under

CFB conditions, the following conclusions could be drawn:

(1) Under the same conditions, the reduction effect of sawdust pyrolysis gas on N_2O was better than that of rice husk and orange peel;

(2) N_2O decomposition was restrained by oxygen content when the flue gas increased from 1% to 8% and improved by the reaction when the temperature increased from 1073.15 K to 1273.15 K;

(3) With the increase of injected sawdust pyrolysis gas, N_2O reduction rate was increased, among which 1.35% was converted into NO, while 0.0075% was converted into NO_2 .

This work was supported by the National Natural Science Foundation of China (50976032), the National High Technology Research and Development of China (2008AA05Z302), the National Basic Research Program of China (2009CB219801), the Key Project of Ministry of Education of China (108033, 107119), Nature Science Foundation of Beijing (3101001), Fundamental Research Funds for the Central Universities (09ZG03) and Doctoral Program of North China Electric Power University (200822015).

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